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Thermodynamic Stability Conditions as an Eigenvalues Fundamental Problem

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Abstract

Quadratic forms diagonalization methods can be used in addressing the stability of physical systems. Thermodynamic stability conditions appears as an eigenvalues fundamental problem, in particular when postulational approaches is taken. The second-order derivatives or appropriate relations between such derivatives of the energy, entropy or any considered thermodynamic potential, as Helmholtz, enthalpy and Gibbs, have interesting mathematical features that directly imply in the physical stability, obtained by use and as consequence of analytical techniques. Formal aspects on the thermal and mechanical stability become simple consequences, but no less formal, of the superposition of rigorously established physical laws, and appropriate applications of mathematical techniques.

Keywords: quadratic forms, Taylor's series, thermodynamic stability, eigenvalues, thermodynamic potentials

1. Introduction

In physics, there is a time-independent theory, namely, thermodynamics that is used to determine the macroscopic equilibrium of physical systems. In practice, to compute the equilibrium conditions and the physical properties of a system, a physicist must find a function that completely describes the system, being capable of capturing all involved properties. The existence of such a function arises as a postulate of the thermodynamics, having an extremum to the equilibrium states [1]. The function is called entropy and has a maximum at final equilibrium state. On the other hand, the same understanding about the physical properties of the system can be extracted through another relevant physical function, namely, energy. This treatment of using energy function instead of entropy to investigate the physical properties is completely equivalent but now the energy has a minimum and its existence also occurs by postulational reason, as for entropy function. A broad discussion on thermodynamic's postulates can be found in Ref. [1].

In practical problems, it would be impossible to computing the total energy of a system taking all time-dependent freedom degrees, such as atomic coordinates of the components of the system each with its translational, rotation energies, etc., among others time-dependent properties. The thermodynamics theory emerges from the fact that a great number of those freedom degrees are eliminated by considering statistical averages, and not macroscopically manifesting. Thus, as the physical principle of energy conservation keeps unaltered over decades, having

been already rigorously tried and confirmed, a well-defined thermodynamic energy function appears somewhat intuitive. Indeed, the energy must be interpreted as a function capable of providing the macroscopic properties of the system. Besides, due to the complexity in measuring the energy of a system, it is relevant to assume some state whereby the energy is arbitrary defined as zero and measuring the energy in connection that state because only energy differences have any physical meaning [1–3].

There are equivalent approaches to investigate the thermodynamics properties of a system in terms of thermodynamic functions (or thermodynamic potentials) of Helmholtz, enthalpy and Gibbs instead of the energy or entropy. Such thermodynamic potentials are obtained by using Legendre transformations in order to change the original extensive variables, or part of them, in the function thermodynamic energy by the intensive variables. Besides, other thermodynamic functions (in addition to those already mentioned) can appear when making Legendre transformations in specific extensive parameters of the energy or in the extensive parameters of the entropy, such as grand canonical potential, and Massieu, Planck and Krammers functions. The function to be used must be defined by the practical characteristics of the problem and these last mentioned functions are less common in more elementary approaches of postulational thermodynamics [1, 4].

A solid understanding of postulational thermodynamic theory is necessary in order to investigate the thermal or mechanic stability of the most diverse systems. The increase in the thermal stability of DNA against thermal denaturation can be experimentally investigated using a methodology in which the differences or changes in the standard values of negativity and positivity of enthalpy and entropy, or even between them, are decisive for the study's conclusions [5]. The formalism of free energy (or Helmholtz potential) can be used for practical determination of the level of stored energy accumulated in material during plastic processing applied as well as the stored energy for the simple stretching of austenitic steel [6]. There are an infinity of applications of thermodynamic theory in which the stability of a system is intimately related to some physical feature of thermodynamic functions, and whose the convenience of the choice is determined by practical situation.

Interesting formalisms or analytical techniques that combine the superposition of the thermodynamic theory and mathematical methods appear as support for problems of applied physics aimed to investigate the stability conditions of a system, either through experimental or computational studies. In order to show of a physical point of view, as arises the thermal and mechanical stability of a system, let us invoke the known physical origin of the energy U , i. e., its existence is determined by a postulate and the same way we know that U is a function of the extensive parameters, entropy S , volume V and the mole numbers of the chemical components N_1, N_2, \dots, N_r . This physical consideration can be mathematically written as $U = U(S, V, N_1, N_2, \dots, N_r)$. Similarly, entropy S is a function of the extensive parameters, energy U , volume V and the mole numbers of the chemical components N_1, N_2, \dots, N_r , and so $S = S(U, V, N_1, N_2, \dots, N_r)$ [1].

In this chapter, we discuss in details the postulate of maximum entropy or minimum energy through which it is possible to see that the thermodynamic functions S or U , or any potential/function derived them by Legendre transformations, have mathematical features that can be obtained of an eigenvalues fundamental problem, that is, the diagonalization of the hypersurfaces defined by $U = U(S, V, N_1, N_2, \dots, N_r)$ or $S = S(U, V, N_1, N_2, \dots, N_r)$ that conveniently expanded in Taylor's series provides the signs its second-order derivatives in an

$(r + 2)$ -dimensional thermodynamic space. Besides, some relations between these derivatives by diagonalization of the quadratic form of U , S or other thermodynamic function, naturally appear and as consequence relevant conclusions about the system stability. Quadratic forms appear in several physical problems, especially in quantum mechanics [7], and in thermodynamic theory this is not different. In particular, we precisely investigate the mathematical characteristics of the hypersurface of energy and other thermodynamic functions for a system of single chemical component. In this case, it is possible to reduce the hypersurface $U(S, V, N_1, N_2, \dots, N_r)$, in an $(r + 2)$ -dimensional thermodynamic space, to a three dimensional hypersurface where $U = U(S, V, N)$ (see that $r = 1$). Analytical calculations of quadratic forms diagonalization are used to reveal the signs of the second-order derivatives of the three-dimensional thermodynamic functions. Accordingly, the stability conditions are obtained.

This chapter is organized as follows. In Section 2, we discuss the general procedures to diagonalize the thermodynamic energy as well as obtain Taylor's series in an $(r + 2)$ -dimensional thermodynamic space. It is also presented the same way to entropy function. In Section 3, we diagonalize thermodynamic energy in a three-dimensional space, and derived Helmholtz, enthalpy, and Gibbs potentials as well as grand canonical potential. In addition, the signs of second-order derivatives of such thermodynamic functions are calculated. In Section 4, stability conditions are presented as consequences of the obtained signs in previous section. As it turns, we summarize our main findings and draw some perspectives in Section 5.

2. The quadratic form of the energy hypersurface in an $(r + 2)$ -dimensional thermodynamic space

We already addressed in the introduction about the postulational existence of the thermodynamic energy function $U = U(S, V, N_1, N_2, \dots, N_r)$ that is a function on extensive parameters entropy S , volume V and the mole numbers of the chemical components N_1, N_2, \dots, N_r , where r represents the amount of chemical components in the system. Besides, U is capable of describing all thermodynamic macroscopic properties of treated system. A formal discussion on extensive parameters can be found in Ref. [1]. However, understand them as those are dependent on the amount of matter or mass of the system.

Remembering the most general form of Taylor's series for a function $f = f(x_1, x_2, \dots, x_n)$ of n variables expanded around $(x_{10}, x_{20}, \dots, x_{n0})$ [8]:

$$f(x_1, x_2, \dots, x_n) = f(x_{10}, x_{20}, \dots, x_{n0}) + \sum_i \frac{\partial f}{\partial x_i} \Delta x_i + \frac{1}{2!} \sum_i \sum_j \frac{\partial^2 f}{\partial x_i \partial x_j} \Delta x_i \Delta x_j + \dots, \quad (1)$$

where $\Delta x_i = x_i - x_{i0}$, and all partial derivatives are evaluated at $(x_{10}, x_{20}, \dots, x_{n0})$. Here x_{i0} denotes the coordinates of some arbitrary stationary point around which the function is expanded, with zero index to differentiate it from all other points in the n -dimensional space.

Let us carefully expanding the energy $U(S, V, N_1, N_2, \dots, N_r)$ using Taylor's series given by Eq. (1) around $(S_0, V_0, N_{10}, N_{20}, \dots, N_{r0})$ point in $(r + 2)$ -dimensional space.

$$\begin{aligned}
 U(S, V, N_1, N_2, \dots, N_r) = & U(S_0, V_0, N_{10}, N_{20}, \dots, N_{r0}) + \frac{\partial U}{\partial S}(S - S_0) \\
 & + \frac{\partial U}{\partial V}(V - V_0) + \sum_{k=1}^r \frac{\partial U}{\partial N_k}(N_k - N_{k0}) + \frac{1}{2!} \left[\frac{\partial^2 U}{\partial S^2}(S - S_0)^2 + \frac{\partial^2 U}{\partial V^2}(V - V_0)^2 \right. \\
 & \left. + \sum_{k=1}^r \frac{\partial^2 U}{\partial N_k^2}(N_k - N_{k0})^2 + \sum_i \sum_{j(i \neq j)} \frac{\partial^2 U}{\partial X_i \partial X_j} \Delta X_i \Delta X_j \right] + \dots,
 \end{aligned} \quad (2)$$

where $\Delta X_i \equiv X_i - X_{i0}$, with $X_i = S, V, N_1, N_2, \dots, N_r$ and $X_{i0} = S_0, V_0, N_{10}, N_{20}, \dots, N_{r0}$. Notice that last term that explicitly appears in Eq. (2) in which the simplified notation X_i is introduced represents all possible combinations of double partial derivatives obtained from the extensive variables of the energy. Besides, see that $i \neq j$ in the same term due to already computed previous terms to $i = j$.

By analogy with the one-variable differential calculus and due to the postulate of minimum energy ($d^2U > 0$, see Refs. [1–3]), taking a stationary point $(S_0, V_0, N_{10}, N_{20}, \dots, N_{r0})$, we know that all first-order derivatives in Eq. (2) are null at this point

$$\frac{\partial U}{\partial S} = 0, \frac{\partial U}{\partial V} = 0 \text{ and } \frac{\partial U}{\partial N_k} = 0 \text{ with } k = (1, \dots, r), \quad (3)$$

and therefore

$$\begin{aligned}
 U(S, V, N_1, N_2, \dots, N_r) = & U(S_0, V_0, N_{10}, N_{20}, \dots, N_{r0}) + \frac{1}{2!} \left[\frac{\partial^2 U}{\partial S^2}(S - S_0)^2 \right. \\
 & \left. + \frac{\partial^2 U}{\partial V^2}(V - V_0)^2 + \sum_{k=1}^r \frac{\partial^2 U}{\partial N_k^2}(N_k - N_{k0})^2 + \sum_i \sum_{j(i \neq j)} \frac{\partial^2 U}{\partial X_i \partial X_j} \Delta X_i \Delta X_j \right] + \dots
 \end{aligned} \quad (4)$$

Let us define in Eq. (4) $\Delta S \equiv S - S_0$, $\Delta V \equiv V - V_0$, $\Delta N_k \equiv N_k - N_{k0}$, $\Delta U \equiv U(S, V, N_1, N_2, \dots, N_r) - U(S_0, V_0, N_{10}, N_{20}, \dots, N_{r0})$, and also $\tilde{U} \equiv 2!(\Delta U)$. Thus, it is possible rewriting Eq. (4) as follows.

$$\begin{aligned}
 \tilde{U}(S, V, N_1, N_2, \dots, N_r) = & \frac{\partial^2 U}{\partial S^2}(\Delta S)^2 + \frac{\partial^2 U}{\partial V^2}(\Delta V)^2 + \sum_{k=1}^r \frac{\partial^2 U}{\partial N_k^2}(\Delta N_k)^2 \\
 & + \sum_i \sum_{j(i \neq j)} \frac{\partial^2 U}{\partial X_i \partial X_j} \Delta X_i \Delta X_j + \dots
 \end{aligned} \quad (5)$$

Notice that \tilde{U} in above expression must be interpreted the same way as the U , being only mathematically multiplied and suppressed by the constants $2!$ and $U(S_0, V_0, N_{10}, N_{20}, \dots, N_{r0})$, respectively. Physically, \tilde{U} also obeys minimum energy postulate and keep the dependence with the extensive parameters, $\tilde{U} = \tilde{U}(S, V, N_1, N_2, \dots, N_r)$. On the other words, \tilde{U} is the original energy function U , at less than a multiplicative constant, and additive. We should not forget that the expression given by Eq. (5) has more terms than those explicitly listed, with third-order, fourth-order derivatives and so on. However, if we take only terms until the second-order derivatives, it is possible to see that hypersurface defined by \tilde{U} is a complete quadratic form, in an $(r + 2)$ -dimensional thermodynamic space (see quadratic forms in Refs. [8, 9]). Then, some mathematical generalities can be extracted of the thermodynamic energy written as Eq. (6) below:

$$\begin{aligned}\tilde{U} = & \frac{\partial^2 U}{\partial S^2}(\Delta S)^2 + \frac{\partial^2 U}{\partial V^2}(\Delta V)^2 \\ & + \sum_{k=1}^r \frac{\partial^2 U}{\partial N_k^2}(\Delta N_k)^2 + \sum_i \sum_{j(i \neq j)} \frac{\partial^2 U}{\partial X_i \partial X_j} \Delta X_i \Delta X_j.\end{aligned}\quad (6)$$

The matricial form of the quadratic expression in Eq. (6) is given by

$$\tilde{U} = (\Delta S \ \Delta V \ \Delta N_1 \ \Delta N_2 \ \dots \ \Delta N_r) \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \dots & \dots & \dots & \dots \\ \vdots & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial X_i \partial X_j} & \vdots & \vdots \\ & & \frac{\partial^2 U}{\partial N_1^2} & & \\ \vdots & \frac{\partial^2 U}{\partial X_j \partial X_i} & & \ddots & \vdots \\ \cdot & \dots & \dots & \dots & \frac{\partial^2 U}{\partial N_r^2} \end{pmatrix} \begin{pmatrix} \Delta S \\ \Delta V \\ \Delta N_1 \\ \Delta N_2 \\ \vdots \\ \Delta N_r \end{pmatrix}, \quad (7)$$

where the second-order derivatives above and below of main diagonal represent all combinations of double partial derivatives in relation to the extensive variables of the energy. Explicitly showing the terms of mixed partial derivatives in the matricial equation given by Eq. (7), we have

$$\tilde{U} = (\Delta S \ \Delta V \ \Delta N_1 \ \Delta N_2 \ \dots \ \Delta N_r) \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial N_1} & \dots & \frac{\partial^2 U}{\partial S \partial N_r} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial V \partial N_1} & \dots & \frac{\partial^2 U}{\partial V \partial N_r} \\ \frac{\partial^2 U}{\partial N_1 \partial S} & \frac{\partial^2 U}{\partial N_1 \partial V} & \frac{\partial^2 U}{\partial N_1^2} & \dots & \frac{\partial^2 U}{\partial N_1 \partial N_r} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial N_r \partial S} & \frac{\partial^2 U}{\partial N_r \partial V} & \frac{\partial^2 U}{\partial N_r \partial N_1} & \dots & \frac{\partial^2 U}{\partial N_r^2} \end{pmatrix} \begin{pmatrix} \Delta S \\ \Delta V \\ \Delta N_1 \\ \Delta N_2 \\ \vdots \\ \Delta N_r \end{pmatrix}. \quad (8)$$

Resuming the previous discussion in which the extensive variables are compactly defined as X_i , we can also express the energy in Eq. (8) of a compact way

$$\tilde{U} = (\Delta X_i)^T M (\Delta X_i), \quad (9)$$

where

$$M \equiv \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial N_1} & \dots & \frac{\partial^2 U}{\partial S \partial N_r} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial V \partial N_1} & \dots & \frac{\partial^2 U}{\partial V \partial N_r} \\ \frac{\partial^2 U}{\partial N_1 \partial S} & \frac{\partial^2 U}{\partial N_1 \partial V} & \frac{\partial^2 U}{\partial N_1^2} & \dots & \frac{\partial^2 U}{\partial N_1 \partial N_r} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial N_r \partial S} & \frac{\partial^2 U}{\partial N_r \partial V} & \frac{\partial^2 U}{\partial N_r \partial N_1} & \dots & \frac{\partial^2 U}{\partial N_r^2} \end{pmatrix}, \quad (10)$$

ΔX_i is a column vector with $\Delta S, \Delta V, \Delta N_1, \dots, \Delta N_r$ components, and ΔX_i^T is the transpose of ΔX_i . As M is a symmetric matrix, a diagonalization procedure can be applied to simplify the investigation of mathematical features of \tilde{U} and its physical consequences. At first, the choice to expanding the thermodynamic energy in Taylor's series up to the second-order is due to the appearance of a complete quadratic form with a known mathematics of many-variable calculus. Accordingly, the canonical form $\tilde{U} = \Delta X_i'^T D \Delta X_i'$ obtained by diagonalization allows visualizing interesting physical features more easily. Notice that D is the eigenvalues matrix of M with $(r+2)$ -components, and the $\Delta X_i'$ is the column eigenvector (with $\Delta S', \Delta V', \Delta N'_1, \dots, \Delta N'_r$ components) of the diagonal matrix D as well as $\Delta X'^T$ is the transpose. A review on quadratic forms diagonalization can be found in Ref. [9]. The canonical form to \tilde{U} can be expressed by Eq. (11)

$$\begin{aligned} \tilde{U} &= (\Delta X_i')^T D (\Delta X_i') = \\ &= \begin{pmatrix} \Delta S' & \Delta V' & \Delta N'_1 & \Delta N'_2 & \dots & \Delta N'_r \end{pmatrix} \begin{pmatrix} \lambda_S & 0 & 0 & 0 & 0 \\ 0 & \lambda_V & 0 & 0 & 0 \\ 0 & 0 & \lambda_{N_1} & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & \lambda_{N_r} \end{pmatrix} \begin{pmatrix} \Delta S' \\ \Delta V' \\ \Delta N'_1 \\ \Delta N'_2 \\ \vdots \\ \Delta N'_r \end{pmatrix} \quad (11) \\ &= \lambda_S (\Delta S')^2 + \lambda_V (\Delta V')^2 + \lambda_{N_1} (\Delta N'_1)^2 + \dots + \lambda_{N_r} (\Delta N'_r)^2. \end{aligned}$$

See that in the canonical form of \tilde{U} given by Eq. (11) are eliminated the mixed partial derivatives of Eq. (6). Besides, the minimum energy postulate imposes to the function $\tilde{U}(S, V, N_1, N_2, \dots, N_r)$ in Eq. (11) the following mathematical condition:

$$\tilde{U} = \lambda_S (\Delta S')^2 + \lambda_V (\Delta V')^2 + \lambda_{N_1} (\Delta N'_1)^2 + \dots + \lambda_{N_r} (\Delta N'_r)^2 > 0. \quad (12)$$

It is possible to see that this condition occurs only when $\lambda_S > 0, \lambda_V > 0, \lambda_{N_1} > 0, \dots, \lambda_{N_r} > 0$ for any sets of values of $\Delta S', \Delta V', \Delta N'_1, \dots, \Delta N'_r$. To obtain the λ_i ($i = S, V, N_1, \dots, N_r$) eigenvalues, it is necessary diagonalize M (see Eq. (8)) by solving the equation $(\lambda_i I - M)X_i = 0$, where I is an identity matrix (see Ref. [9]) that provides the determinant below

$$\begin{vmatrix} \left(\frac{\partial^2 U}{\partial S^2} - \lambda \right) & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial N_1} & \dots & \frac{\partial^2 U}{\partial S \partial N_r} \\ \frac{\partial^2 U}{\partial V \partial S} & \left(\frac{\partial^2 U}{\partial V^2} - \lambda \right) & \frac{\partial^2 U}{\partial V \partial N_1} & \dots & \frac{\partial^2 U}{\partial V \partial N_r} \\ \frac{\partial^2 U}{\partial N_1 \partial S} & \frac{\partial^2 U}{\partial N_1 \partial V} & \left(\frac{\partial^2 U}{\partial N_1^2} - \lambda \right) & \dots & \frac{\partial^2 U}{\partial N_1 \partial N_r} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial N_r \partial S} & \frac{\partial^2 U}{\partial N_r \partial V} & \frac{\partial^2 U}{\partial N_r \partial N_1} & \dots & \left(\frac{\partial^2 U}{\partial N_r^2} - \lambda \right) \end{vmatrix} = 0. \quad (13)$$

Observe that Eq. (13) implies an equation in λ of $(r + 2)$ -degree. Besides, all λ_i are necessarily positive due to the minimum energy postulate.

So far, we have show some generalities about thermodynamic energy in an $(r + 2)$ -dimensional space. Notice that diagonalizing M by solving Eq. (13) is not an easy task. For a system with great number of chemical components analytical solutions of Eq. (13) can become increasingly hard.

If we take the entropy of the system instead of energy, all above formalism remains valid by simple exchanging U and S variables in the equations. In addition, due to the maximum entropy postulate, all eigenvalues of second-order derivatives matrix (similar to M by exchanging U and S) must be negatives ($\lambda_U < 0$, $\lambda_V < 0$, $\lambda_{N_1} < 0$, ..., $\lambda_{N_r} < 0$). Then, in this case we have Eq. (14) instead Eq. (12).

$$\tilde{S} = \lambda_S(\Delta U')^2 + \lambda_V(\Delta V')^2 + \lambda_{N_1}(\Delta N'_1)^2 + \dots + \lambda_{N_r}(\Delta N'_r)^2 < 0. \quad (14)$$

In a two-dimensional thermodynamic space, a discussion on the eigenvalues of M and the physical consequences of its positivity is presented in Ref. [10]. In this case, the conditions of thermal and mechanical stability are naturally demonstrated through the signs of the second-order derivatives of some thermodynamic function of two-variables. The two-dimensional problem arises when is considered a one-component system and, in particular, we can take the thermodynamic energy per mol, reducing the dependence of such energy function for only the variables entropy (s) and volume (v) per mol ($u = u(s, v)$).

The stability conditions of a thermodynamic system are intrinsically related to the signs of the second-order derivatives of the energy, being the exact calculating of the eigenvalues of Eq. (13) (of previously known signs) an important factor in order to understand the physical origin of the stability of the system. In next section, we present a discussion of eigenvalues of the energy in a three-dimensional thermodynamic space.

3. Diagonalization of the energy in a three-dimensional thermodynamic space

Let us define the energy in a three-dimensional thermodynamic space. To do this, we consider a system with one chemical component and explicitly write the energy $U = U(S, V, N)$ in terms of the involved extensive parameters S , V and N . Similarly of Eq. (3) and by analogy with one-variable calculus, we have $\frac{\partial U}{\partial S} = \frac{\partial U}{\partial V} = \frac{\partial U}{\partial N} = 0$ (at a stationary point (S_0, V_0, N_0)) due to the minimum energy principle. Besides, in order to investigate the second-order derivatives of U (or \tilde{U} , there are no physical difference), a simple matricial quadratic form can be obtained by application of Eqs. (6), (7) and (8), as follows:

$$\tilde{U} = (\Delta S \ \Delta V \ \Delta N) \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial N} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial V \partial N} \\ \frac{\partial^2 U}{\partial N \partial S} & \frac{\partial^2 U}{\partial N \partial V} & \frac{\partial^2 U}{\partial N^2} \end{pmatrix} \begin{pmatrix} \Delta S \\ \Delta V \\ \Delta N \end{pmatrix} = (\Delta X_i)^T M_{(3 \times 3)} (\Delta X_i), \quad (15)$$

where

$$M_{(3 \times 3)} = \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial N} \\ \frac{\partial^2 U}{\partial V \partial S} & \frac{\partial^2 U}{\partial V^2} & \frac{\partial^2 U}{\partial V \partial N} \\ \frac{\partial^2 U}{\partial N \partial S} & \frac{\partial^2 U}{\partial N \partial V} & \frac{\partial^2 U}{\partial N^2} \end{pmatrix} \quad (16)$$

ΔX_i is a column vector with ΔS , ΔV , ΔN components, ΔX_i^T is the transpose of ΔX_i , and $M_{(3 \times 3)}$ is a symmetric matrix that provides three eigenvalues for \tilde{U} by diagonalization of $M_{(3 \times 3)}$. Thus, by using the canonical form of \tilde{U} combined with minimum energy principle, we know that all signs of the eigenvalues λ_1 , λ_2 , and λ_3 of $M_{(3 \times 3)}$ are positive

$$\begin{aligned} \tilde{U} &= (\Delta X_i')^T D_{(3 \times 3)} (\Delta X_i') = (\Delta S' \ \Delta V' \ \Delta N') \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \begin{pmatrix} \Delta S' \\ \Delta V' \\ \Delta N' \end{pmatrix} \\ &= \lambda_1 (\Delta S')^2 + \lambda_2 (\Delta V')^2 + \lambda_3 (\Delta N')^2 > 0. \end{aligned} \quad (17)$$

Note that $D_{(3 \times 3)}$ in Eq. (17) is the eigenvalues matrix of $M_{(3 \times 3)}$ given by Eq. (16). As in Eq. (13), here we need solve the eigenvalues equation $(\lambda I_{(3 \times 3)} - M_{(3 \times 3)})X_i = 0$ that provides the following determinant

$$\begin{vmatrix} \left(\frac{\partial^2 U}{\partial S^2} - \lambda \right) & \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial S \partial N} \\ \frac{\partial^2 U}{\partial V \partial S} & \left(\frac{\partial^2 U}{\partial V^2} - \lambda \right) & \frac{\partial^2 U}{\partial V \partial N} \\ \frac{\partial^2 U}{\partial N \partial S} & \frac{\partial^2 U}{\partial N \partial V} & \left(\frac{\partial^2 U}{\partial N^2} - \lambda \right) \end{vmatrix} = 0. \quad (18)$$

The determinant given by Eq. (18) provides a third-degree equation in λ .

$$\begin{aligned} & -\lambda^3 + \left[\frac{\partial^2 U}{\partial S^2} + \frac{\partial^2 U}{\partial V^2} + \frac{\partial^2 U}{\partial N^2} \right] \lambda^2 + \left[\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} + \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial N^2} + \frac{\partial^2 U}{\partial V^2} \frac{\partial^2 U}{\partial N^2} + \frac{\partial^2 U}{\partial S \partial N} \frac{\partial^2 U}{\partial N \partial S} \right. \\ & + \frac{\partial^2 U}{\partial V \partial N} \frac{\partial^2 U}{\partial N \partial V} + \frac{\partial^2 U}{\partial S \partial V} \frac{\partial^2 U}{\partial V \partial S} \left. \right] \lambda + \left[\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} \frac{\partial^2 U}{\partial N^2} + \frac{\partial^2 U}{\partial S \partial V} \frac{\partial^2 U}{\partial V \partial N} \frac{\partial^2 U}{\partial N \partial S} \right. \\ & + \frac{\partial^2 U}{\partial V \partial S} \frac{\partial^2 U}{\partial N \partial V} \frac{\partial^2 U}{\partial S \partial N} - \frac{\partial^2 U}{\partial N \partial V} \frac{\partial^2 U}{\partial V \partial N} \frac{\partial^2 U}{\partial S^2} - \frac{\partial^2 U}{\partial N \partial S} \frac{\partial^2 U}{\partial S \partial N} \frac{\partial^2 U}{\partial V^2} \\ & \left. - \frac{\partial^2 U}{\partial S \partial V} \frac{\partial^2 U}{\partial V \partial S} \frac{\partial^2 U}{\partial N^2} \right] = 0. \end{aligned} \quad (19)$$

The above equation is commonly known as characteristic equation, and its solution necessarily imply in three positive roots due to the minimum energy postulate. After some algebraic manipulations [8, 11, 12] in order to solve Eq. (19) and considering $\lambda_1 > 0$, $\lambda_2 > 0$ and $\lambda_3 > 0$ (three positive roots), we find the following relations

$$\frac{\partial^2 U}{\partial S^2} > 0, \frac{\partial^2 U}{\partial V^2} > 0, \frac{\partial^2 U}{\partial N^2} > 0 \text{ (as expected from one – variable calculus),} \quad (20)$$

$$\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \frac{\partial^2 U}{\partial S \partial V} \frac{\partial^2 U}{\partial V \partial S} > 0, \quad (21)$$

$$\left[\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} \frac{\partial^2 U}{\partial N^2} + \frac{\partial^2 U}{\partial S \partial V} \frac{\partial^2 U}{\partial V \partial N} \frac{\partial^2 U}{\partial N \partial S} + \frac{\partial^2 U}{\partial V \partial S} \frac{\partial^2 U}{\partial N \partial V} \frac{\partial^2 U}{\partial S \partial N} - \frac{\partial^2 U}{\partial N \partial V} \frac{\partial^2 U}{\partial V \partial N} \frac{\partial^2 U}{\partial S^2} - \frac{\partial^2 U}{\partial N \partial S} \frac{\partial^2 U}{\partial S \partial N} \frac{\partial^2 U}{\partial V^2} - \frac{\partial^2 U}{\partial S \partial V} \frac{\partial^2 U}{\partial V \partial S} \frac{\partial^2 U}{\partial N^2} \right] > 0. \quad (22)$$

Observe that Eq. (22) is equivalent to the determinant of $M_{(3 \times 3)}$ (see Eq. (16)), being positive to energy representation, and so $|M_{(3 \times 3)}| > 0$. Besides, considering that the product of the three roots $x_1 x_2 x_3 = -d/a$ in a general third-degree equation $ax^3 + bx^2 + cx + d = 0$ is a known expression of more elementary courses, Eq. (22) can be easily obtained due to the positivity of all eigenvalues of \tilde{U} (see that d is the last bracket term in Eq. (19), and $a = -1$) in the condition of minimum introduced by the thermodynamic postulate. In addition, notice that first relation in Eq. (19) is the determinant of the upper left 1×1 submatrix of $M_{(3 \times 3)}$, while Eq. (20) is the determinant of the upper left 2×2 submatrix of $M_{(3 \times 3)}$.

In short, to obtaining in which conditions at equilibrium point (S_0, V_0, N_0) $\tilde{U} = \tilde{U}(S, V, N)$ has a minimum in this three-dimensional thermodynamic space, the set of relations given by Eqs. (20)-(22) must occur, where the relations $\frac{\partial^2 U}{\partial V^2} > 0$ and $\frac{\partial^2 U}{\partial N^2} > 0$ in Eq. (20) were introduced for a more physical than mathematical reason during analytical solution of Eq. (19). A general approach about mathematical second derivative test for many variable functions can be found in Ref. [8].

We must solve Eq. (19) permuting U and S in an equivalent entropy representation. Besides, by imposing all negative values due to maximum entropy postulate, it is possible to obtain a set of relations as in Eqs. (20)-(22). Solving eigenvalues equation below

$$\begin{aligned} & -\lambda^3 + \left[\frac{\partial^2 S}{\partial U^2} + \frac{\partial^2 S}{\partial V^2} + \frac{\partial^2 S}{\partial N^2} \right] \lambda^2 + \left[\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} + \frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial N^2} + \frac{\partial^2 S}{\partial V^2} \frac{\partial^2 S}{\partial N^2} + \frac{\partial^2 S}{\partial U \partial N} \frac{\partial^2 S}{\partial N \partial U} \right. \\ & + \frac{\partial^2 S}{\partial V \partial N} \frac{\partial^2 S}{\partial N \partial V} + \frac{\partial^2 S}{\partial U \partial V} \frac{\partial^2 S}{\partial V \partial U} \left. \right] \lambda + \left[\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} \frac{\partial^2 S}{\partial N^2} + \frac{\partial^2 S}{\partial S \partial V} \frac{\partial^2 S}{\partial V \partial N} \frac{\partial^2 S}{\partial N \partial U} \right. \\ & + \frac{\partial^2 S}{\partial V \partial U} \frac{\partial^2 S}{\partial N \partial V} \frac{\partial^2 S}{\partial U \partial N} - \frac{\partial^2 S}{\partial N \partial V} \frac{\partial^2 S}{\partial V \partial N} \frac{\partial^2 S}{\partial U^2} - \frac{\partial^2 S}{\partial N \partial U} \frac{\partial^2 S}{\partial U \partial N} \frac{\partial^2 S}{\partial V^2} \\ & \left. - \frac{\partial^2 S}{\partial U \partial V} \frac{\partial^2 S}{\partial V \partial U} \frac{\partial^2 S}{\partial N^2} \right] = 0, \end{aligned} \quad (23)$$

and imposing $\lambda_1 < 0$, $\lambda_2 < 0$ and $\lambda_3 < 0$ (all negative eigenvalues due to maximum entropy postulate), we obtain

$$\frac{\partial^2 S}{\partial U^2} < 0, \frac{\partial^2 S}{\partial V^2} < 0, \frac{\partial^2 S}{\partial N^2} < 0 \text{ (as expected from one - variable calculus)} \quad (24)$$

$$\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} - \frac{\partial^2 S}{\partial U \partial V} \frac{\partial^2 S}{\partial V \partial U} > 0 \quad (25)$$

$$\left[\frac{\partial^2 S}{\partial U^2} \frac{\partial^2 S}{\partial V^2} \frac{\partial^2 S}{\partial N^2} + \frac{\partial^2 S}{\partial U \partial V} \frac{\partial^2 S}{\partial V \partial N} \frac{\partial^2 S}{\partial N \partial U} + \frac{\partial^2 S}{\partial V \partial U} \frac{\partial^2 S}{\partial N \partial V} \frac{\partial^2 S}{\partial U \partial N} - \frac{\partial^2 S}{\partial N \partial V} \frac{\partial^2 S}{\partial V \partial N} \frac{\partial^2 S}{\partial U^2} - \frac{\partial^2 S}{\partial N \partial U} \frac{\partial^2 S}{\partial U \partial N} \frac{\partial^2 S}{\partial V^2} - \frac{\partial^2 S}{\partial U \partial V} \frac{\partial^2 S}{\partial V \partial U} \frac{\partial^2 S}{\partial N^2} \right] < 0. \quad (26)$$

As it happened for energy, here Eq. (24) is expected from one-variable calculus and its last two relations were introduced for a more physical than mathematical reason during analytical solution of Eq. (23). It is important to emphasize that although Eq. (25) keeps the same format and sign of Eq. (21), the sign in Eq. (26) for the entropy formalism is now negative. This should not cause any surprise and can be concluded even without explicitly calculate the three eigenvalues of characteristic equation due to the known expression to the product between the three roots, $x_1 x_2 x_3 = -d/a$ in a general third-degree equation $ax^3 + bx^2 + cx + d = 0$. Then, as all eigenvalues are now negative, Eq. (26) is easily verified from characteristic equation (see Eq. (23) where d is the last bracket term, and $a = -1$). The set of Eqs. (24)-(26) provides the mathematical conditions of maximum for entropy thermodynamic function $\tilde{S} = \tilde{S}(U, V, N)$ at (U_0, V_0, N_0) .

Some physical problems require the use of thermodynamic potentials of Helmholtz, enthalpy and Gibbs as well as the grand canonical potential instead of thermodynamic energy to be more easily solved. These thermodynamic functions are introduced in the next topic.

3.1 Second-order derivatives of other thermodynamic functions

By using Legendre transformations, it is possible to change the extensive variables, or part of them, in the thermodynamic energy function. In this subsection, we are considering the same energy of three extensive variables defined by $U = U(S, V, N)$ in which making appropriate Legendre transformations the intensive variables are introduced. A discussion on extensive and intensive thermodynamic variables can be found in Ref. [1]. Legendre's transformation is, in short, a process of change of variables.

3.1.1 Helmholtz potential

In order to introduce Helmholtz potential that is an energy function that instead of being a function of S , V and N it is written in terms of T , V and N , we need to make Legendre transformation (change S by T) in extensive parameter S . This process of introducing intensive parameter T is described below. Before let us write $U(S, V, N)$ as

$$dU(S, V, N) = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN, \quad (27)$$

where the temperature can be defined by $T \equiv \frac{\partial U}{\partial S}$ with V and N constant, the pressure is defined by $P \equiv -\frac{\partial U}{\partial V}$ with S and N constant, and the chemical potential is defined by $\mu \equiv \frac{\partial U}{\partial N}$ with S and V constant. With these definitions, we have to Eq. (27)

$$dU = TdS - PdV + \mu dN. \quad (28)$$

Taking

$$\begin{aligned} d(TS) &= TdS + SdT \\ TdS &= d(TS) - SdT, \end{aligned} \quad (29)$$

and substituting Eq. (29) into Eq. (28)

$$\begin{aligned} dU &= d(TS) - SdT - PdV + \mu dN \\ d(U - TS) &= -SdT - PdV + \mu dN \\ dF &= -SdT - PdV + \mu dN, \end{aligned} \quad (30)$$

where

$$F \equiv U - TS (\text{being } F \text{ known as Helmholtz potential}). \quad (31)$$

See of the Eq. (30) that F is a function of T , V and N . Then $F = F(T, V, N)$, and the energy F defined as function of T , V and N has modified its concavity in relation to the new introduced parameter by Legendre transformation in S , i. e., the second-order derivatives of F on T is negative now, keeping positive the signs of F on V and N as in original energy (see Eq. (32) below).

$$\frac{\partial^2 F}{\partial T^2} < 0, \quad \frac{\partial^2 F}{\partial V^2} > 0, \quad \frac{\partial^2 F}{\partial N^2} > 0. \quad (32)$$

It is a general fact that Legendre transformation change the sign of the second-order derivatives of the new introduced function in relation that intensive parameter. A demonstration of this consideration to molar Helmholtz potential $f = f(s, v)$ is shown in Re. [10], and a treatment on Legendre transformations can be found in Ref. [13]. Recently, the thermodynamic stability of chignolin protein was theoretically investigated by using of a computational methodology of decomposition of the Helmholtz energy profile that indicates that intramolecular interactions predominantly stabilized certain conformations of the protein [14]. Besides, in the same study the direct Helmholtz energy decomposition provides the predominant factor in the thermodynamic stability of proteins.

Following the same procedure used to derive the stability conditions of the energy and entropy functions, it is possible to obtain a complete set of relations that Helmholtz potential must obey. Mathematically F is known as a saddle surface. This feature of F stems from the imposition that some eigenvalue of the canonical form of F (similarly to the Eq. (17)) have opposite sign to the others. The saddle surface of Helmholtz of three variables has a maximum in relation to the temperature but a minimum in relation to the volume and mole number. The relations given by Eq. (32) are sufficient to conclude on the physical stability of a system, as demonstrated in Section 4, and the other expressions to the second-order derivatives of F are not shown here. However, the curious reader can be computing all signs of the second-order derivatives to Helmholtz and to other thermodynamic functions that follow below, as already discussed to energy and entropy functions.

3.1.2 Enthalpy potential

The enthalpy potential is also mathematically a saddle surface. In this case, Legendre transformation is applied in the extensive parameter V and introduced

the intensive parameter P . Further, H keep unaltered with a minimum in relation to the entropy S and N but becomes a maximum on P , and so $H = H(S, P, N)$. Remembering that $dU = TdS - PdV + \mu dN$, then

$$\begin{aligned} d(pV) &= PdV + VdP \\ -PdV &= -d(PV) + VdP, \end{aligned} \quad (33)$$

and substituting Eq. (33) into Eq. (28), we have

$$\begin{aligned} dU &= TdS - d(PV) + VdP + \mu dN \\ d(U + PV) &= TdS + VdP + \mu dN \\ dH &= TdS + VdP + \mu dN, \end{aligned} \quad (34)$$

where

$$H \equiv U + PV \text{ (being } H \text{ known as enthalpy potential)}. \quad (35)$$

Due to Legendre transformations, it is possible to conclude that

$$\frac{\partial^2 H}{\partial S^2} > 0, \quad \frac{\partial^2 H}{\partial P^2} < 0, \quad \frac{\partial^2 H}{\partial N^2} > 0, \quad (36)$$

and other inequalities can be obtained the same way as previously presented to energy and entropy functions, i. e., by diagonalization of $H(S, P, N)$.

3.1.3 Gibbs potential

It is possible to write a function obtained by double Legendre transformation in the extensive parameters S and V , namely Gibbs potential. This is a function on introduced intensive variables T and P . To do that, we combine Eqs. (29) and (33) into Eq. (28). Then,

$$\begin{aligned} dU &= TdS - PdV + \mu dN \\ dU &= d(TS) - SdT - d(PV) + VdP + \mu dN \\ dU - d(TS) + d(PV) &= -SdT + VdP + \mu dN \\ d(U - TS + PV) &= -SdT + VdP + \mu dN \\ dG &= -SdT + VdP + \mu dN, \end{aligned} \quad (37)$$

where

$$G \equiv U - TS + PV \text{ (being } G \text{ known as Gibbs potential)}. \quad (38)$$

Legendre transformations provide the following relations, and $G = G(T, P, N)$ as seen in Eq. (37).

$$\frac{\partial^2 G}{\partial T^2} < 0, \quad \frac{\partial^2 G}{\partial P^2} < 0, \quad \frac{\partial^2 G}{\partial N^2} > 0. \quad (39)$$

Here the second-order derivatives in relation to T and P are negative now as well as the $G = G(T, P, N)$ becomes a surface of maximum in relation of these two

parameters. See that energy keeps unaltered in relation to N , and Gibbs potential has a minimum in relation to mole number because Legendre transformations are applied only in S and V , introducing T and P respectively. Besides, by diagonalization of quadratic form obtained by expanding of G , it is possible to compute other inequalities in addition those expressed by Eq. (39), as already discussed to the energy and entropy formalisms.

3.1.4 Grand canonical potential

A function of T , V and μ is known as grand canonical potential J . To obtaining $J = J(T, V, \mu)$ let us introduce the intensive parameter μ of the extensive parameter N as follows. Taking

$$\begin{aligned} d(\mu N) &= Nd\mu + \mu dN \\ \mu dN &= d(\mu N) - Nd\mu, \end{aligned} \quad (40)$$

and combining the above equation with Eq. (29) into (28), we have

$$\begin{aligned} dU &= TdS - PdV + \mu dN \\ dU &= d(TS) - SdT - PdV + d(\mu N) - Nd\mu \\ dU - d(TS) - d(\mu N) &= -SdT - PdV - Nd\mu \\ d(U - TS - \mu N) &= -SdT - PdV - Nd\mu \\ dJ &= -SdT - PdV - Nd\mu, \end{aligned} \quad (41)$$

where

$$J = U - TS - \mu N = F - \mu N (\text{being } J \text{ known as grand canonical potential}). \quad (42)$$

Thus, by Legendre transformations in S and N , T and μ intensive variables are introduced, respectively, the relations below are naturally obtained.

$$\frac{\partial^2 J}{\partial T^2} < 0, \frac{\partial^2 J}{\partial V^2} > 0, \frac{\partial^2 J}{\partial \mu^2} < 0. \quad (43)$$

These relations indicate that G has now a maximum in relation to intensive parameters T and μ , keeping a minimum on V . Legendre transformations applied in the entropy formalism are also useful to derive other thermodynamic functions that are not treated here. The appropriate choice of the thermodynamic function is relevant in practical problems. Besides, thermodynamic functions are convex functions of their extensive variables (positive signs of the second-order derivatives) and concave functions (negative signs of the second-order derivatives) of their intensive variables [1].

Novel geometric approaches aimed at obtaining thermodynamic relations in a systematic way for a number of thermodynamic potentials and formally derived the classical Gibbs stability condition has been recently investigated [15].

So far, we demonstrate the mathematical conditions that second-order derivatives of the thermodynamic functions must satisfied. In the next section, we use these conditions to directly obtain the mechanical and thermal stability of a general system.

4. The stability conditions of a system

Let us start this section remembering some quantities of physical interest defined below [1–3]:

$$\alpha \equiv \frac{1}{V} \frac{\partial V}{\partial T} \quad (44)$$

$$c_V \equiv \frac{T}{N} \frac{\partial S}{\partial T} \quad (45)$$

$$c_P \equiv \frac{T}{N} \frac{\partial S}{\partial T} \quad (46)$$

$$k_T \equiv -\frac{1}{V} \frac{\partial V}{\partial P} \quad (47)$$

$$k_S \equiv -\frac{1}{V} \frac{\partial V}{\partial P}, \quad (48)$$

where α (at p constant) in Eq. (44) is the coefficient of thermal expansion, c_V and c_P in Eqs. (45) and (46) respectively, are the specific heats at V or P constant, k_T (T constant) in Eq. (47) is the isothermal compressibility and k_S (S constant) in Eq. (48) is the adiabatic compressibility. All these quantities are relevant in physical applications and their exact values as well as their increase or decrease tendencies can say a lot about the stability of the physical system.

The thermal expansion is related to changes in dimensions of physical systems due to temperature variations. We can understand the behavior of materials on the macroscopic or microscopic scale when subjected to temperature changes by the absolute values of α that can be positive or negative.

Specific heats are useful to understand the thermal properties of physical systems in several length scales (macroscale and microscale). Besides, the specific heats are positive physical quantities associated to the thermal stability of the system, as will be mathematically demonstrated in this section.

The isothermal and adiabatic compressibilities are positive physical quantities, being related to the mechanical stability of the system. A deep comprehension of the physical origin of the mentioned quantities in terms of the signs of the second-order derivatives of thermodynamis functions, it is relevant to theoretical or experimental researchers.

In order to better investigate the physical consequences of the signs of the second-order derivatives of the energy, see the first relation in Eq. (20)

$$\frac{\partial^2 U}{\partial S^2} > 0. \quad (49)$$

Remembering the temperature definition $T = \frac{\partial U}{\partial S}$, we have by derivation of temperature T side by side in relation to the S entropy

$$\frac{\partial T}{\partial S} = \frac{\partial^2 U}{\partial S^2} > 0. \quad (50)$$

Then, if we combine Eq. (50) and the definition of specific heat (at V constant) given by Eq. (45), it is possible to obtain

$$\begin{aligned} \frac{T}{Nc_V} &= \frac{\partial^2 U}{\partial S^2} > 0 \\ \Rightarrow c_V &> 0. \end{aligned} \quad (51)$$

A positive specific heat ($c_V > 0$) is obtained due to the absolute temperature is positive. Besides, N is a positive amount. The same physical conclusion can be obtained of the first relation in Eq. (32), $\frac{\partial^2 F}{\partial T^2} < 0$. As F is a function of T , V and N ($F = F(T, V, N)$), an infinitesimal of dF is given by

$$dF = \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial V} dV + \frac{\partial F}{\partial N} dN \quad (52)$$

that compared with Eq. (30) provides

$$-S = \frac{\partial F}{\partial T}, \quad (53)$$

$$-P = \frac{\partial F}{\partial V}, \quad (54)$$

and

$$\mu = \frac{\partial F}{\partial N}. \quad (55)$$

If we take the derivation side by side of Eq. (53) in relation to T considering V and N constant

$$-\frac{\partial S}{\partial T} = \frac{\partial^2 F}{\partial T^2}. \quad (56)$$

It is possible to observe that the left side of Eq. (56) is related to the specific heat at V constant and the sign of the second-order derivatives can be checked by comparing with Eq. (32), and so

$$-\frac{\partial S}{\partial T} = \frac{\partial^2 F}{\partial T^2} < 0, \quad (57)$$

and from definition of specific heat in Eq. (45)

$$-\frac{Nc_V}{T} < 0 \Rightarrow \frac{Nc_v}{T} > 0 \Rightarrow c_v > 0. \quad (58)$$

Note that Eq. (58) represents the same result already obtained in Eq. (51), only taking different formalisms to thermodynamic function, and so analyzing distinct second-order derivatives. The specific heat must be interpreted as the necessary amount of heat to increase or decrease the temperature of the physical system. A negative specific heat would imply in an inexistent physical situation because we would have a system capable of receiving some quantity of heat (positive) and decreasing its temperature (negative dT). There is still another non-physical situation with negative specific heat in the hypothetical situation in which the system loses heat but increases its temperature.

We investigate now the signs of second-order derivatives of Gibbs potential. The relation given by first inequality in Eq. (39) provides an important conclusion to specific heat at P constant, with $c_P > 0$. To demonstrate that, let us take a differential element dG of Gibbs potential $G = G(T, P, N)$

$$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP + \frac{\partial G}{\partial N} dN. \quad (59)$$

The above equation can be compared with Eq. (37), and we obtain

$$-S = \frac{\partial G}{\partial T}, \quad (60)$$

$$V = \frac{\partial G}{\partial P}, \quad (61)$$

and

$$\mu = \frac{\partial G}{\partial N}. \quad (62)$$

Deriving Eq. (60) side by side in relation to T at P constant, we have

$$-\frac{\partial S}{\partial T} = \frac{\partial^2 G}{\partial T^2}, \quad (63)$$

and from definition of specific heat at P constant in Eq. (46) and by comparing with the first inequality in Eq. (39)

$$\begin{aligned} -\frac{Nc_P}{T} &= \frac{\partial^2 G}{\partial T^2} < 0 \\ \frac{Nc_P}{T} &> 0 \Rightarrow c_P > 0. \end{aligned} \quad (64)$$

Notice that specific heat at P constant is also positive. The positivity of the specific heats previous shown is related to the thermal stability of the physical system. Then, it is possible to see that the thermal stability emerge as consequence of the signs of the second-order derivatives previously treated. Thus, appropriately computing the eigenvalues of the matricial energy or other thermodynamic function is essential to finding the stability conditions.

Resuming Eq. (54) and by derivation of the left and right sides in relation to V keeping T constant

$$\frac{\partial P}{\partial V} = -\frac{\partial^2 F}{\partial V^2}. \quad (65)$$

Comparing Eq. (66) with the definition to isothermal compressibility in Eq. (47), we can obtain

$$\frac{\partial P}{\partial V} = -\frac{1}{Vk_T}. \quad (66)$$

As the sign of the second-order derivative in Eq. (66) is positive, we have

$$\begin{aligned} -\frac{1}{Vk_T} &= -\frac{\partial^2 F}{\partial V^2} \\ \frac{1}{Vk_T} &= \frac{\partial^2 F}{\partial V^2} > 0 \Rightarrow k_T > 0. \end{aligned} \quad (67)$$

Notice that the sign of the second-order derivative of the appropriately chosen potential leads to a relevant relation for the sign of physical quantity of interest. Besides, in the definition given by Eq. (47) that increments of pressure in the system leads to decrease in volume due to the ever positive isothermal

compressibility, and this is an intuitive conclusion. From Eq. (67) we mathematically demonstrated that isothermal compressibility is always positive due to specific features of the potentials. In particular, the positive value of k_T appears from curvature of some chosen potential. The same way $k_S > 0$ can be obtained from enthalpy potential through the sign of the second relation ($\frac{\partial^2 H}{\partial p^2} < 0$) in Eq. (36), and after some algebraic manipulations. A positive value of this physical quantity is associated with the mechanical stability of the physical system, as in k_T .

It is relevant to clarify that α does not have a positive defined sign that can be obtained from some function. The well-known case of the water shows that volume increases when temperature decreases below at 4°C , being negative α in this regime. Yet, thermodynamic books [1–3] show some relations between the physical quantities, as $c_p = c_v + TV\alpha^2/Nk_T$, $c_p/c_v = k_T/k_S$ as well as $c_p \geq c_v$ and $k_T \geq k_S$ obtained by reduction of thermodynamic derivatives and by using Maxwell's relations. But this is not the purpose of this chapter.

It is worthy of emphasis that some stability condition can be deduced by the signs of the second-order derivatives of energy (or any thermodynamic function), as presented in this chapter. In a three-dimensional (or higher) thermodynamic space the complexity in obtain with success the stability conditions for some potential is associated to the matrix order of the second-order derivatives. Besides, to all cases one or several second-order relations must be manipulated to conclude about the thermal and mechanical stability of the system.

5. Conclusions

In this chapter, we show the useful of specific linear algebra topics in addition with many-variable calculus that coupled to minimum energy postulate appear as in important insight to understand the stability of thermodynamic systems. We find the thermal and mechanical stability of physical systems are directly associated with the signs of the second-order derivatives of thermodynamic energy or other taken representation.

We present a general addressing to the energy representation in terms of matrix equations whereby the stability conditions arise of an eigenvalues fundamental problem. Besides, the minimum energy postulate provides the signs of the second-order derivatives. Accordingly, of a physical point of view the stability of a system occurs due to minimum energy postulate.

Formal characteristics of postulational thermodynamic theory and, particularly, about the second-order derivatives of the thermodynamic functions are discussed with relevant consequences on the thermal and mechanical stability. The presented analytical formalism is an important support to conclude how the stability of a system arises, and can be useful in any field of the exact sciences. We hope that this methodology can be extended to higher-order matrices of energy as well as some of the obtained relations can be used in specific problems of applied physics.

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